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VOLATILES IN INTERPLANETARY DUST PARTICLES

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INTRODUCTION

Interplanetary dust particles (IDPs) collected by specially equipped aircraft flying in the stratosphere have generated a lot of interest during the last decade. These particles, consisting of primitive materials originating in small solar system bodies such as comets and asteroids, are complex heterogeneous species with a variety of components (Mackinnon and Rietmeijer, 1987).

In order to understand the past histories of IDPs, it is particularly important to know the nature of the volatiles present. Gibson and Sommer (1986), Gibson et al. (1989) and Hartmetz et al. (1990, 1991b) have studied volatiles released from a number of IDPs. However, a large number of particles must be studied in order to establish trends, to classify types of IDPs, and to have comparison data for determining the origins of IDPs. This study involves the analysis of six IDPs using laser microprobe-mass spectrometry.

EXPERIMENTAL

Collection and Processing

The six particles in this study were from the Large Area Collector L2005 flown aboard a NASA ER-2 aircraft during a series of flights that were made within west-central North America during the fall of 1989 (Zolensky et al., 1990). The collector was coated with a 20:1 mixture of

silicone oil and freon. It was exposed to the stratosphere at an altitude of 20 km for a total of 40 hours.

The IDPs were processed in an ultraclean (Class-100) laboratory at Johnson Space Center. The six particles in this study were all cluster particles, small pieces of larger, friable particles which fragmented during collection. The particles were removed from the collection flag and rinsed with hexane to remove the silicone oil remaining on the surface from the collection procedure. They were then mounted on small pieces of gold which had been cleaned by placing in an ultrasonic cleaner in a mixture of ethanol and acetone followed by surface cleaning in an oxygen plasma.

Analysis

When particles are removed from the collector, they are classified as cosmic dust, terrestrial contamination (either artificial or natural), aluminum oxide spheres, or uncertain identification based on their morphology from SEM images, elemental composition from EDX spectra, and optical properties. The six composite particles used in this study were all from larger particles classified as cosmic dust (Zolensky et al., 1990). An SEM photomicrograph was taken of each of the six particles, and an energy dispersive X-ray (EDX) analysis was done using a JEOL-35CF Scanning Electron Microscope. All six particles were chondritic. Results of the EDX analysis are shown in Table 1.

A particle was then placed in the sample chamber, and the system was evacuated to a pressure of about 2×10^{-7} torr. The sample was vaporized using a Jarrel Ash Q-switched Nd glass laser, and the mass spectrum of the extracted volatiles was obtained with a Hewlett-Packard 5970 Mass Selective Detector. Due to the small size of the particle, the laser shot extended into the gold, making it necessary to do background subtraction. Several laser shots were then taken into the gold (some near the particle and some on the other side of the piece of gold) to obtain an average background spectrum of the volatiles vaporized from the surface of the gold. This background spectrum was then subtracted from the spectrum of the particle to obtain the true spectrum of volatiles liberated from the particle.

The data were normalized (Hartmetz et al., 1990) in order to compare them with analyses of other IDPs, and only those peaks that were greater than one standard deviation (calculated from the gold measurements) above the background were displayed.

In order to have comparison spectra, samples of meteorites and of known minerals were analyzed in a similar manner.

RESULTS AND DISCUSSION

Meteorites

Hartmetz et al. (1991a) have discussed the volatiles obtained from carbonaceous chondrites. In order to become

familiar with the instrumentation and the system software and to have comparison spectra under similar operating conditions, spectra of Allende and of Murchison were obtained (Figs. 1 and 2). Both Allende and Murchison are carbonaceous chondrites and are rich in volatiles. Hydrocarbons were evident in both spectra. Both samples released CO, O₂, and CO₂; however, amounts from Allende were smaller than from Murchison. Allende released considerably less water than did Murchison. Although both meteorites contain sulfur-bearing species, the samples volatilized in this study contained very little, if any, sulfur.

Minerals

In order to better understand the results from the IDPs, spectra were obtained of azurite, calcite, troilite, and a mixture of the three on gold coated with silicone oil and on gold which had previously been coated with silicone oil but had been rinsed with hexane (Figs 3 - 10). In each instance the appropriate gold background was subtracted from the sample spectrum. Peaks corresponding to C, CO, CO₂, O, O₂, OH, and perhaps H₂O would be expected from azurite, 2CuCO₃·Cu(OH)₂. All of these were observed as strong peaks except OH and H₂O. Perhaps the OH bond is weak enough to be broken by the energy of the laser, giving O and H (although the OH peak is sometimes seen in other spectra). The instrument could not detect elemental hydrogen if it were

present; however, it probably combines with other species such as carbon to make CH , C_2H_2 , etc. The peaks due to silicone oil and hexane residues which remained on the azurite are small (considering the logarithmic scale) and are easily distinguished from peaks from the mineral itself. This tells us that the majority of contaminant peaks in an IDP spectrum do not originate during processing but rather during collection of the particle. During collection and return to earth, the particle apparently absorbs silicone oil which is retained in its structure and is not removed by rinsing with hexane during processing.

The peaks expected in a calcite (CaCO_3) spectrum, C, CO, CO_2 , and O_2 , are present; although they are not as intense as in the azurite spectra.

The sample of troilite may have contained a carbonate and/or a hydrate phase in addition to the iron sulfide. Considerably more hydrocarbon peaks were present in the troilite spectra than in the spectra of the other two minerals. These are probably not due to contaminants because all three minerals were treated the same. The peaks which could result from a sulfur-containing compound are S, H_2S , CS, SO, COS, SO_2 , and CS_2 . These are seen in varying amounts in all the spectra containing troilite and are especially predominate in the spectrum of the mixture on gold rinsed with hexane.

Interplanetary Dust Particles

General Comments

Contaminants associated with collecting and processing the IDPs are evident in all the IDP spectra. Although none of the particles could be considered very volatile-rich, each spectrum contains several peaks not present in the spectra of silicone oil, freon, or hexane (Hartmetz et al., 1990), the three species used during collection and processing of the particles. Some of these peaks could be due to other contaminants; however, species are considered indigenous to the particle if they are not present in the spectra of any of the three compounds used in the collecting and processing steps. Table 2 lists the indigenous volatile species found in the six IDPs studied. Significant peaks are labeled on each spectrum. If one of these species is present, even as a trace component, in any of the contaminants, the label is in parentheses.

These spectra do not contain the large numbers of peaks, particularly those due to hydrocarbons, found in Allende and Murchison. However, a number of the predominant peaks in both meteorites are present in several of the IDPs (C, C₂H₅, groups of hydrocarbons around 40 and in the range from 50 to 60, and high molecular weight aromatic hydrocarbons such as benzene and toluene).

Comparing the IDP spectra to the three minerals studied, there is no clear evidence of the presence of carbonate. Two IDP spectra have large CO₂ peaks, but

neither of these contains CO, and one has a large peak at 28 which could be CO, but it does not contain CO₂. Both CO and CO₂ are usually released from carbonates, as shown in the spectra of azurite and calcite. If the CO and CO₂ do not come from carbonate, it is possible that oxygen comes from a source such as silicate and combines with carbon in the laser plume to produce the oxide.

From the EDX spectra, sulfur is shown to be present in L2005C21, L2005C28, and L2005D27. Comparing these to troilite, a sulfide-bearing mineral, peaks might be expected at 32 (S), 34 (H₂S), 48 (SO), 60 (COS), 64 (SO₂), and 76 (CS₂). None of the spectra contains all of these peaks; however, in each of the three spectra, there are at least two peaks associated with sulfur. It is not possible to determine the exact sulfur-bearing species; however, SO₂ (and maybe even SO₃) would be expected from sulfate. Both of these, along with O₂ (or S), are present in L2005C21, showing the likelihood of a sulfate mineral. L2005C28, on the other hand, does not contain any of these but only COS and CS₂. Gibson and Carr (1989) examined several terrestrial sulfides and showed CS₂ to be the dominant volatile species released. Thus, L2005C28 probably contains a sulfide mineral.

Harmetz et al. (1991) classified IDPs according to the volatiles released. Table 3 lists the six IDPs from the present study according to this classification.

Individual Particles

Particle L2005C21 is a fragment of Particle L2005C17. Its spectrum (Fig. 11) shows the presence of carbon (C), the ethyl group (C_2H_5), and some higher molecular weight hydrocarbons, particularly aromatics such as benzene (C_6H_6) and toluene ($C_6H_5CH_3$). The most predominant peak is 32 which could be either sulfur (S) or oxygen (O_2). The EDX analysis shows that sulfur is present. The peak at 64 is probably due to SO_2 . (This peak is not present in silicone oil, the major contaminant, and is small in both freon and hexane.) If enough oxygen is present, the peak at 80 could possibly be from SO_3 . The peaks at 16 and 32 indicate the likelihood of oxygen; however, the absence of peaks at 28 and 44 shows that carbonate is not present. Silicates or perhaps even sulfates could be the source of the oxygen.

Particle L2005C24 is a fragment of Particle L2005C5. (See Fig. 12.) Peaks at 17 and 18, OH and H_2O , respectively, are indicative of a hydrated species present in the particle. A large peak at 28 often indicates the presence of CO; however, the absence of a peak at 44 (CO_2) means a carbonate source is unlikely. Some CO could be formed as an oxidation product in limited oxygen in the plume created by the laser shot. In this case, C_2H_4 is probably a major contributor to the 28 peak because C_2H_5 and C_2H_6 are also present. Peaks due to benzene (C_6H_6) and toluene ($C_6H_5CH_3$) can also be seen in the spectrum.

Particle L2005C26, a fragment of L2005C1, contains very few volatiles but does show peaks at 12 (C), 13 (CH), and several high masses, indicating the presence of some carbon-bearing species. (See Fig. 13.)

Particle L2005C28 is a fragment of L2005C4. (See Fig. 14.) The peak at 17 (OH) is indicative of a hydrated species. Both aliphatic (fragments such as CH, C₅H₇, and C₇H₁₁) and aromatic hydrocarbons (C₆H₆) are present. The EDX spectrum shows the presence of sulfur. The peaks at 60 and 76 are probably due to COS and CS₂, respectively.

Particle L2005C30 is a fragment of Particle L2005C2. (See Fig. 15.) The peak at 17 (OH) probably comes from some hydrate. The 44 peak indicates CO₂ either produced from carbonate or formed from a reaction of oxygen with carbon-bearing species, as mentioned earlier. The carbon peak is noticeably absent, but a few hydrocarbon species are present.

Particle L2005D27 is a fragment of Particle L2005D1. (See Fig. 16.) Like the previous particle, a CO₂ peak but not a CO peak is present. Carbon (C), ethyl (C₂H₅), and several high molecular weight hydrocarbon species are present. The EDX spectrum indicates the presence of sulfur. The 64 and 76 peaks are probably SO₂ and CS₂, respectively.

CONCLUSION

The six particles studied have very different compositions. They are not very volatile-rich; however,

they all appear to contain carbonaceous material, both aliphatic and aromatic. There is no clear evidence for the presence of carbonates.

The spectra of particles L2005C24, L2005C28, L2005C30, and L2005D27 contain peaks due to OH and/or H_2O . These could come from several sources such as adsorbed water, water of hydration, and hydroxide-bearing minerals.

Without further study it is impossible to tell the origin of specific IDPs. All six of these IDPs contained volatiles which appeared to be indigenous to the particle. Additional study is needed in order to see trends and to classify the particles. The most pressing need is a method of collecting the particles without introducing any contaminant species.

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TABLE 1. EDX Major Element Analysis^a

Particle	Major Components
L2005C21	Si, S, Mg, O, Fe, Ca, Na, Al
L2005C24	Si, Mg, Fe, O, Ca, (Al)
L2005C26	Si, Mg, Fe, O, (Ca), (Al), (Ni)
L2005C28	S, Si, Fe, Mg, O, (Al), (Ni)
L2005C30	Si, Mg, Fe, O, (Ca), (Ti), (Al), (Na)
L2005D27	Si, Mg, O, S, Fe, (Na), (Al), (Ca)

^aElements are listed in order of abundances, and trace amounts are placed in parentheses.

TABLE 2. Indigenous Volatile Species^a

Particle	Volatile Components
L2005C21	C, C ₂ H ₅ , O ₂ or S, SO ₂ , C ₅ H ₆ , C ₆ H ₆ , C ₆ H ₇ , C ₆ H ₅ CH ₃
L2005C24	OH, C ₂ H ₅ , C ₂ H ₆ , C ₄ , C ₄ H, C ₅ H ₈ , C ₅ H ₉ , C ₆ H ₆ , C ₆ H ₅ CH ₃
L2005C26	C, CH, and some high m.w. hydrocarbons
L2005C28	CH, OH, SOH?, C ₅ H ₇ , CS ₂ , C ₆ H ₆ , C ₆ H ₇ , C ₇ H ₁₁
L2005C30	OH, C ₂ H ₅ , C ₂ H ₆ , CO ₂ , Si(OH) ₂ ?, C ₅ H ₈ , C ₅ H ₉
L2005D27	C, C ₂ H ₅ , CO ₂ , SOH?, Si(OH) ₂ ?, SO ₂ , CS ₂ , C ₆ H ₆ , C ₆ H ₇ , C ₆ H ₅ CH ₃ , C ₇ H ₉ , C ₇ H ₁₁ , C ₇ H ₁₆

^aA species is considered indigenous if it is present in the spectrum of the particle and not in the spectra of any of the species used in collecting and processing IDPs (silicone oil, freon, or hexane).

TABLE 3. Classification of IDPs

Relatively Large Amounts of Indigenous Volatiles	Few Volatiles	Sulfur Species	Carbonaceous Material	Hydroxide Bearing
L2005C21	L2005C26	L2005C21	L2005C21	L2005C24
L2005C24		L2005C28	L2005C24	L2005C28
L2005C28		L2005D27	L2005C26	L2005C30
L2005C30			L2005C28	
L2005D27			L2005C30	
			L2005D27	

FIGURES

Notes

Only significant peaks are labeled. On the IDP spectra, labels are in parentheses if the species occur (even in trace amounts) in any of the compounds used in collecting and processing the IDPs.

Error limits are presented on all spectra. On the meteorite spectra, the top of the gray bar represents the average value for that component. The top of the white bar is one standard deviation above the average, and the top of the black bar is one standard deviation below the average. No background was subtracted from the meteorite spectra. The minerals and the IDPs were on gold, and an average gold spectrum was subtracted from the spectrum obtained from the mineral or IDP. On the spectra of the minerals and the IDPs, the top of the gray bar is the value for that component; the top of the white bar is one standard deviation (calculated from the gold background) above the value; and the top of the black bar is one standard deviation below the value.

The figures are mass spectra of the following.

Fig. 1. Allende

Fig. 2. Murchison

Fig. 3. Azurite on Gold Coated with Silicone Oil

Fig. 4. Azurite on Gold Rinsed with Hexane

Fig. 5. Calcite on Gold Coated with Silicone Oil

Fig. 6. Calcite on Gold Rinsed with Hexane

Fig. 7. Troilite on Gold Coated with Silicone Oil

Fig. 8. Troilite on Gold Rinsed with Hexane

Fig. 9. Azurite, Calcite, and Troilite Mixture on Gold Coated with Silicone Oil

Fig. 10. Azurite, Calcite, and Troilite Mixture on Gold Rinsed with Hexane

Fig. 11. Particle L2005C21

Fig. 12. Particle L2005C24

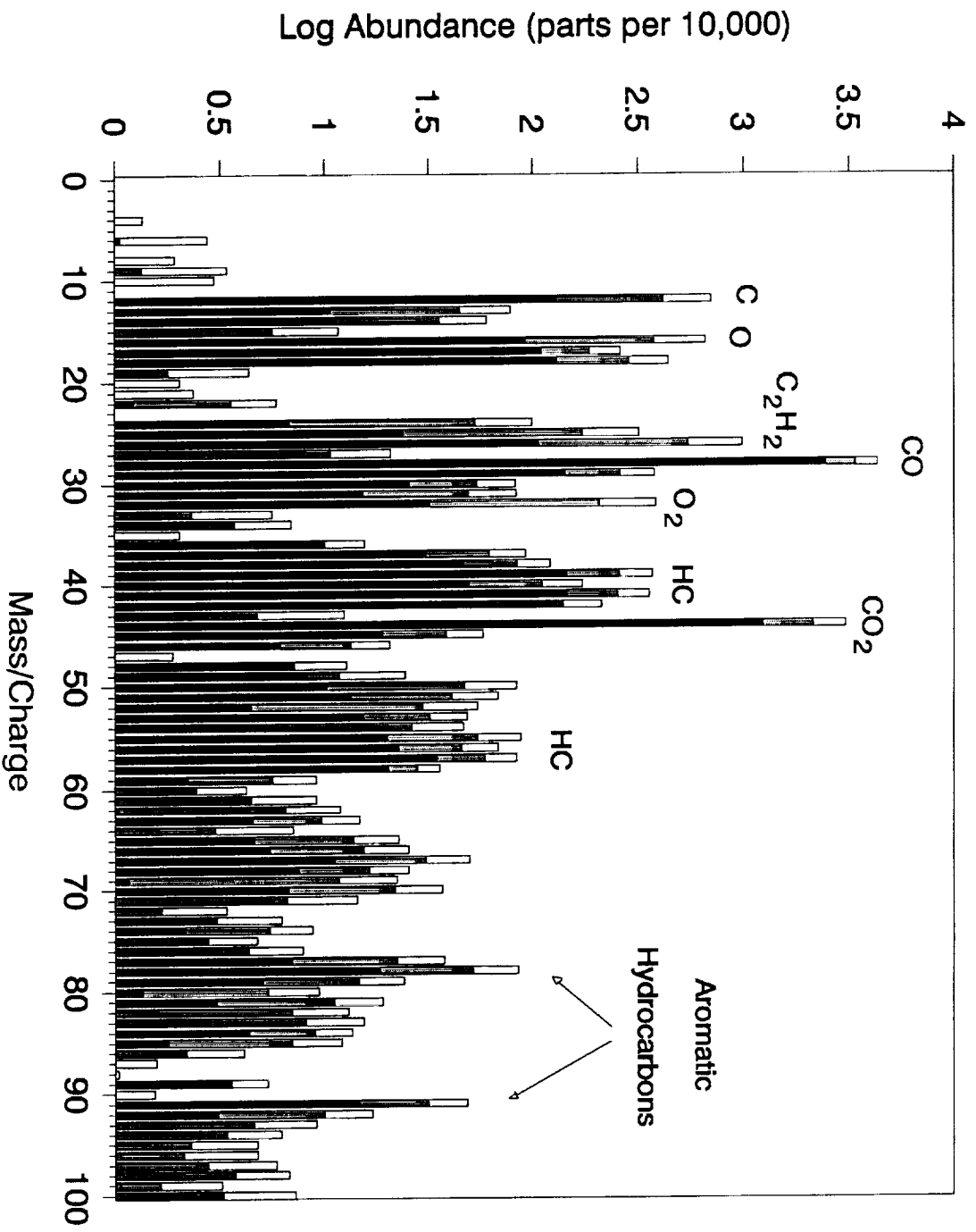
Fig. 13. Particle L2005C26

Fig. 14. Particle L2005C28

Fig. 15. Particle L2005C30

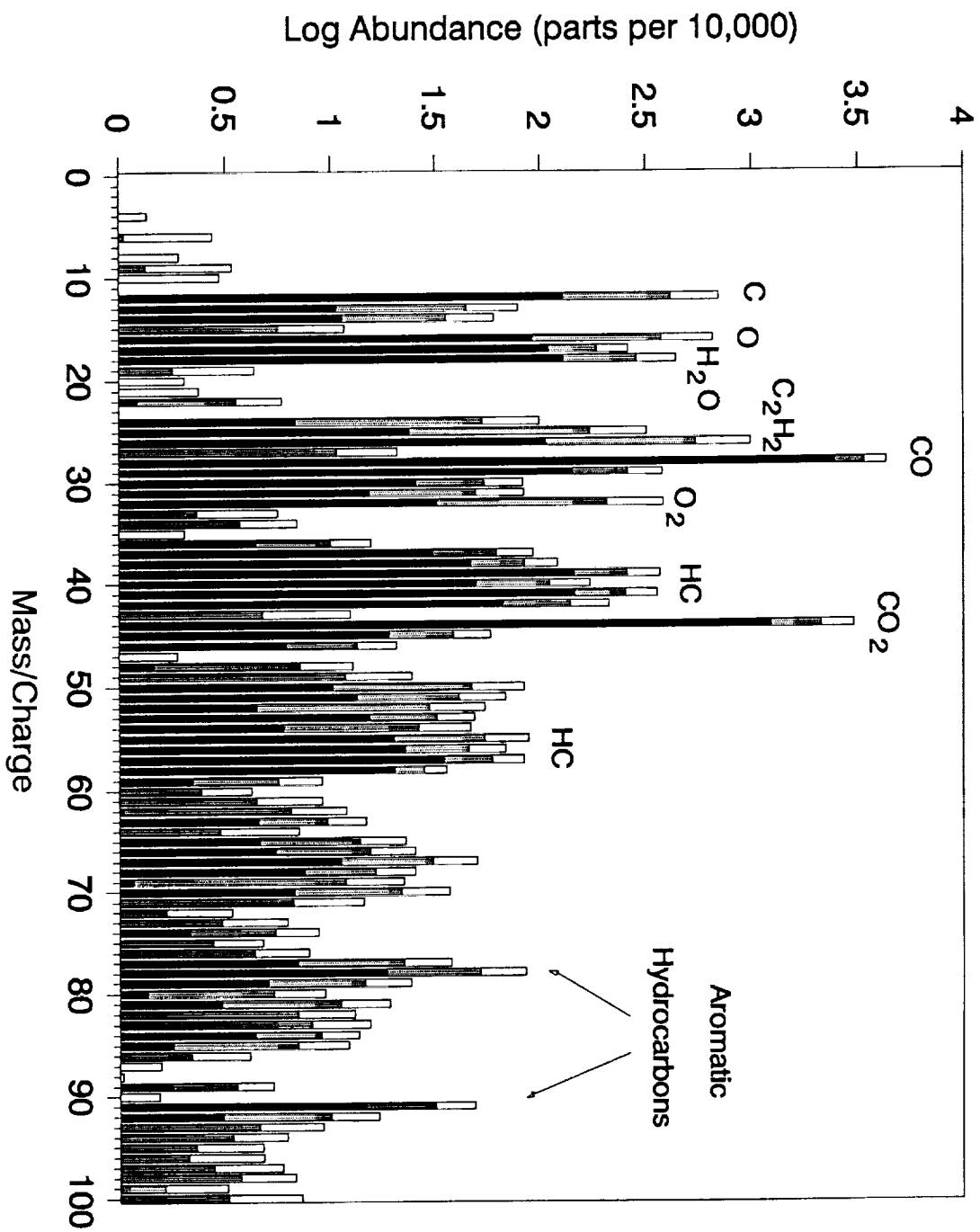
Fig. 16. Particle L2005D27

ALLENDE



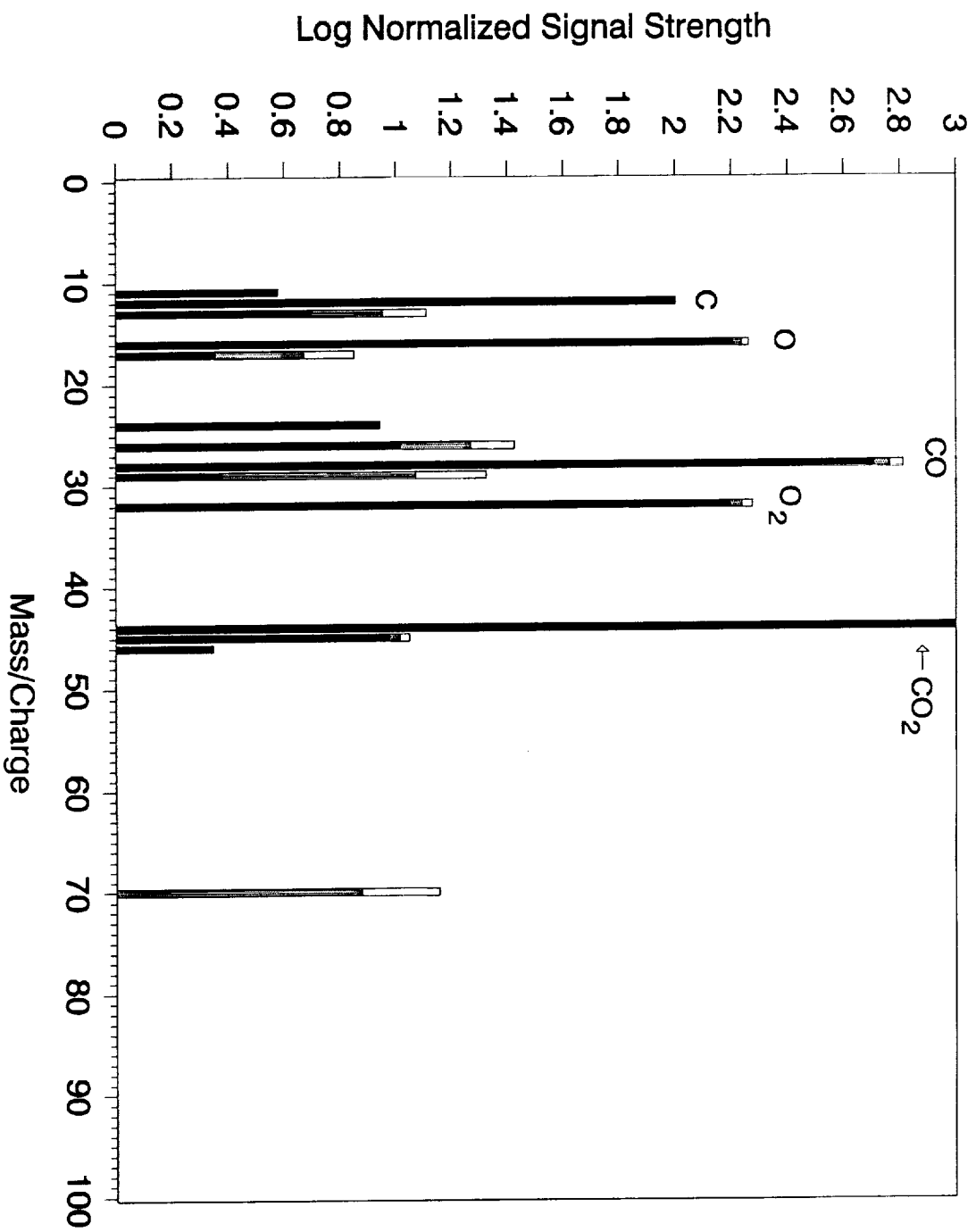
MURCHISON

On Silicone Oil



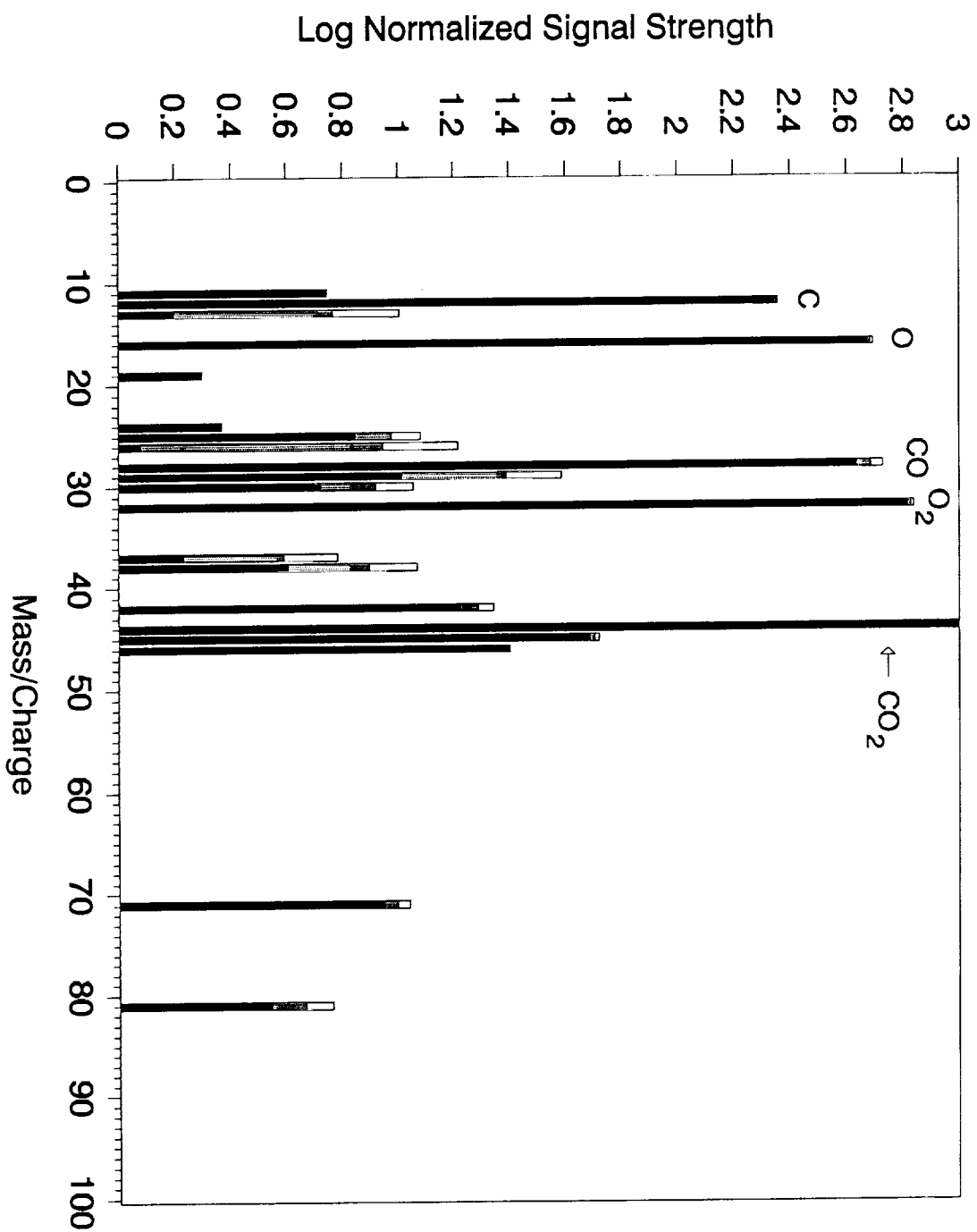
AZURITE

On Gold Coated with Silicone Oil



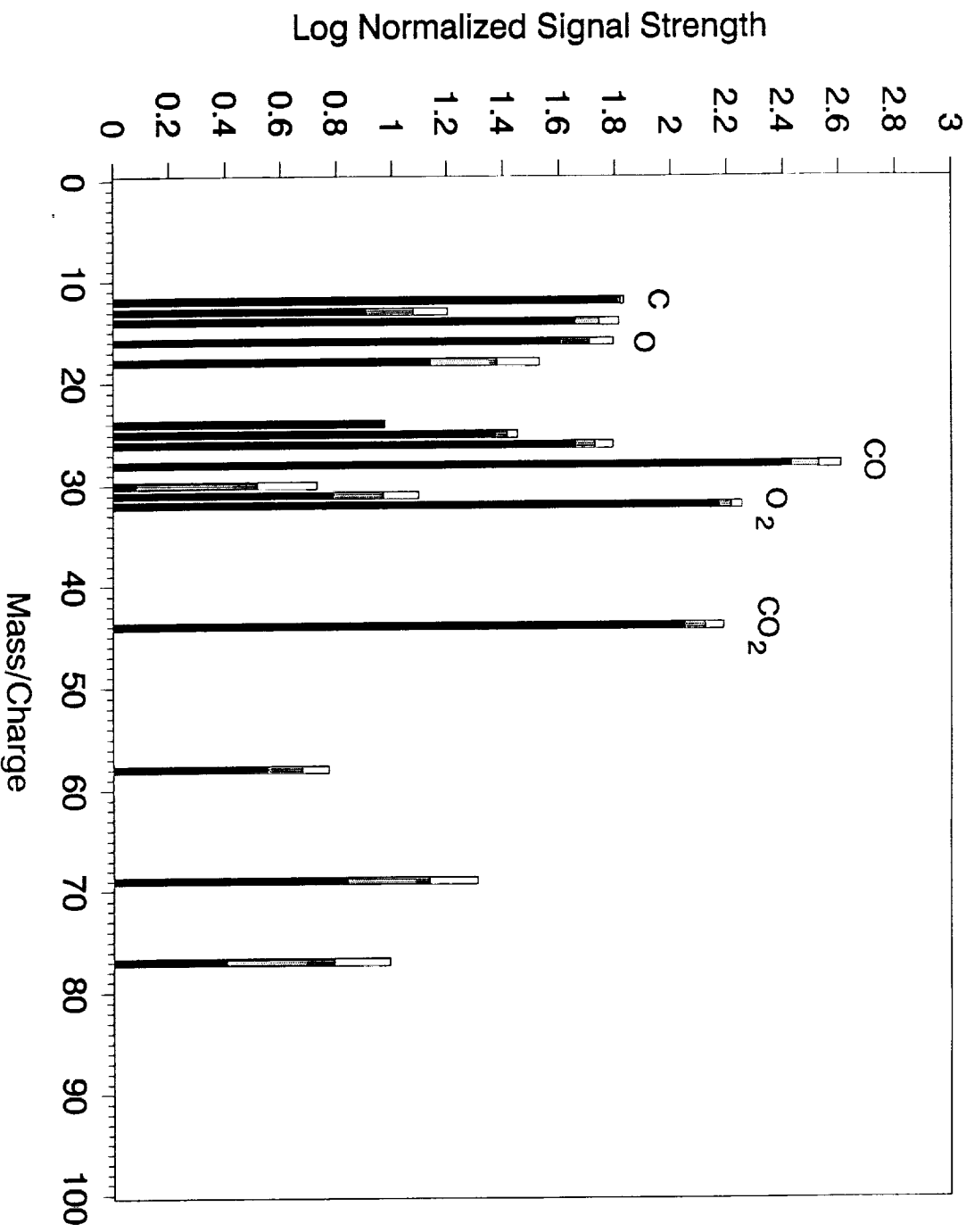
AZURITE

On Gold Rinsed with Hexane



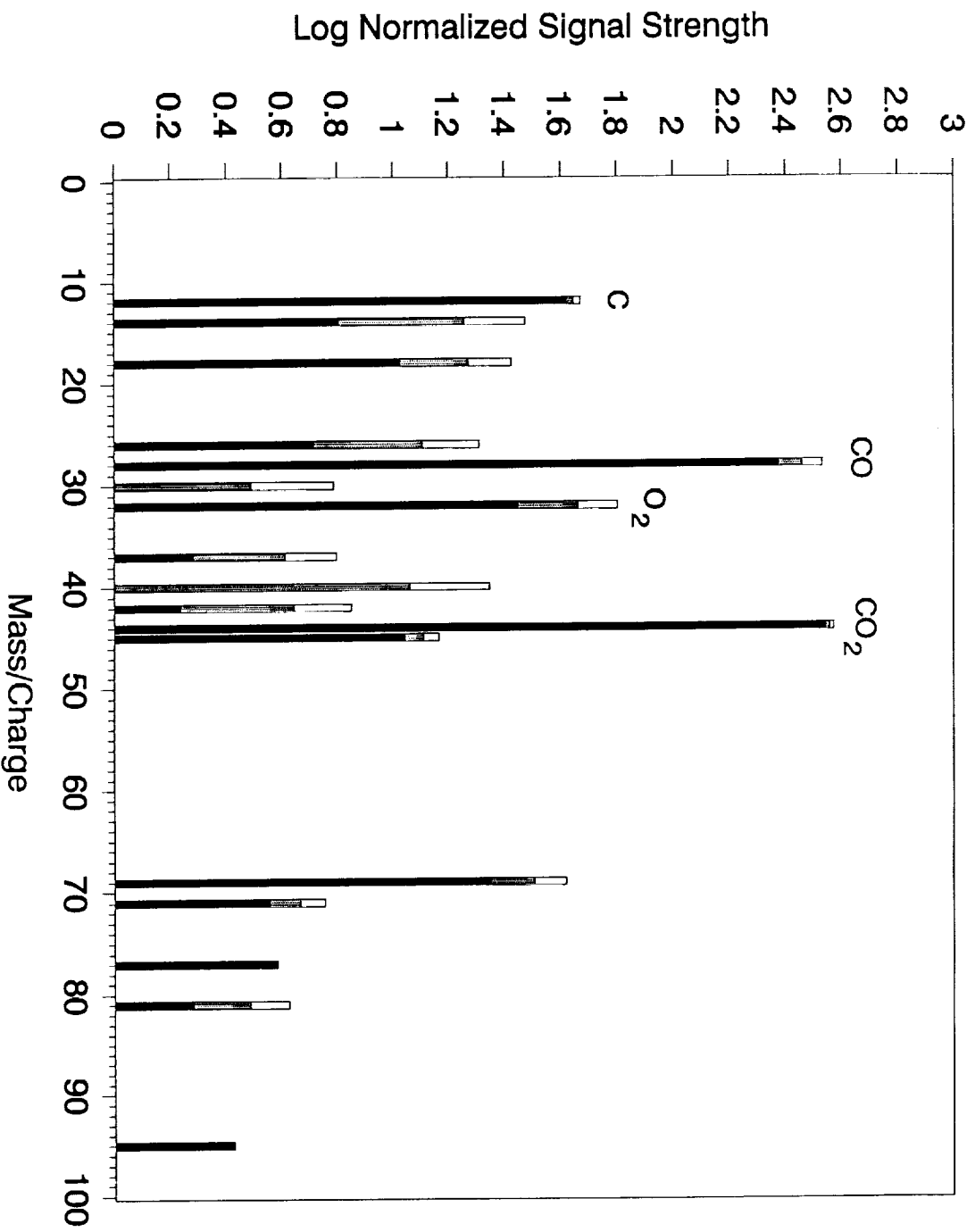
CALCITE

On Gold Coated with Silicone Oil



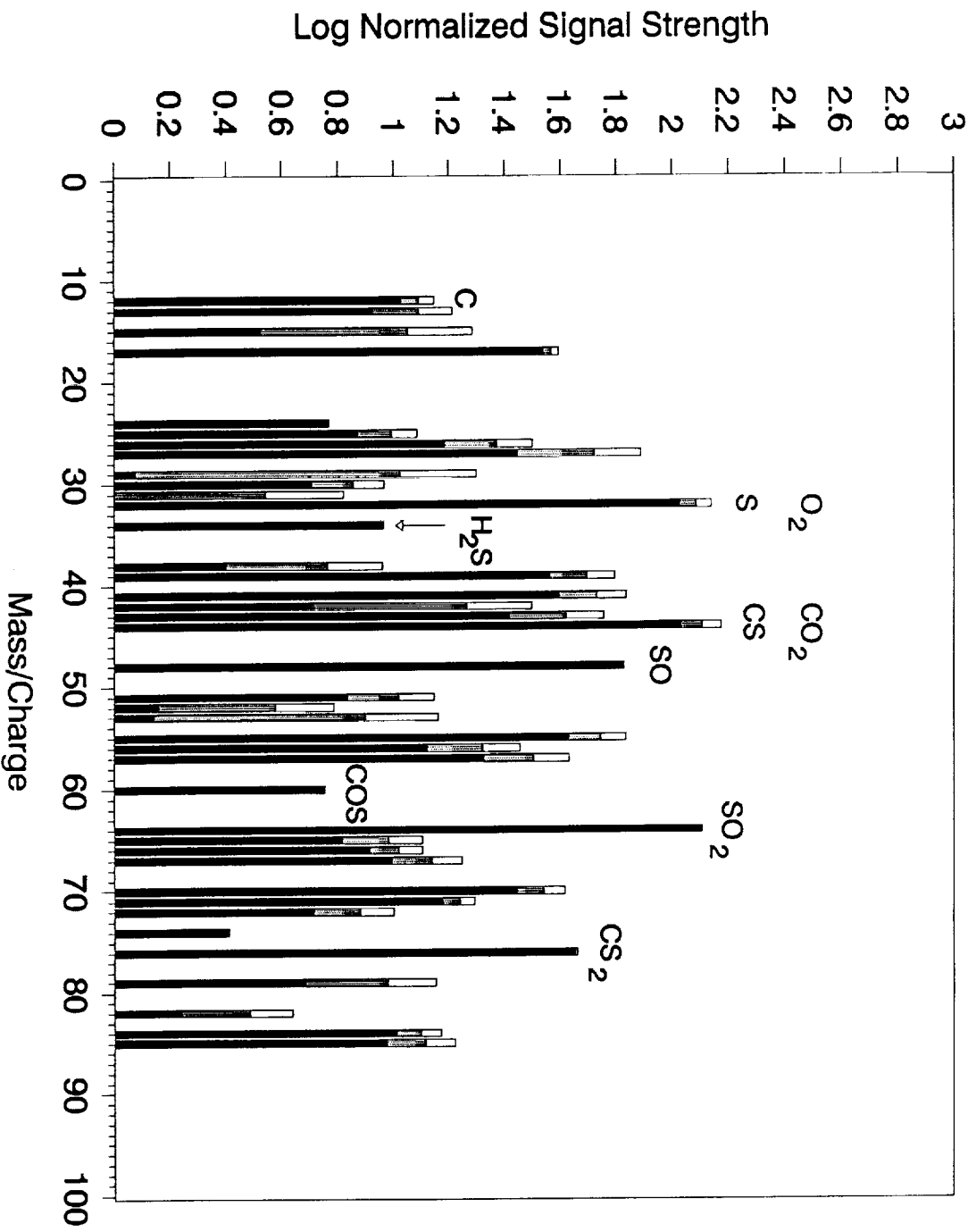
CALCITE

On Gold Rinsed with Hexane



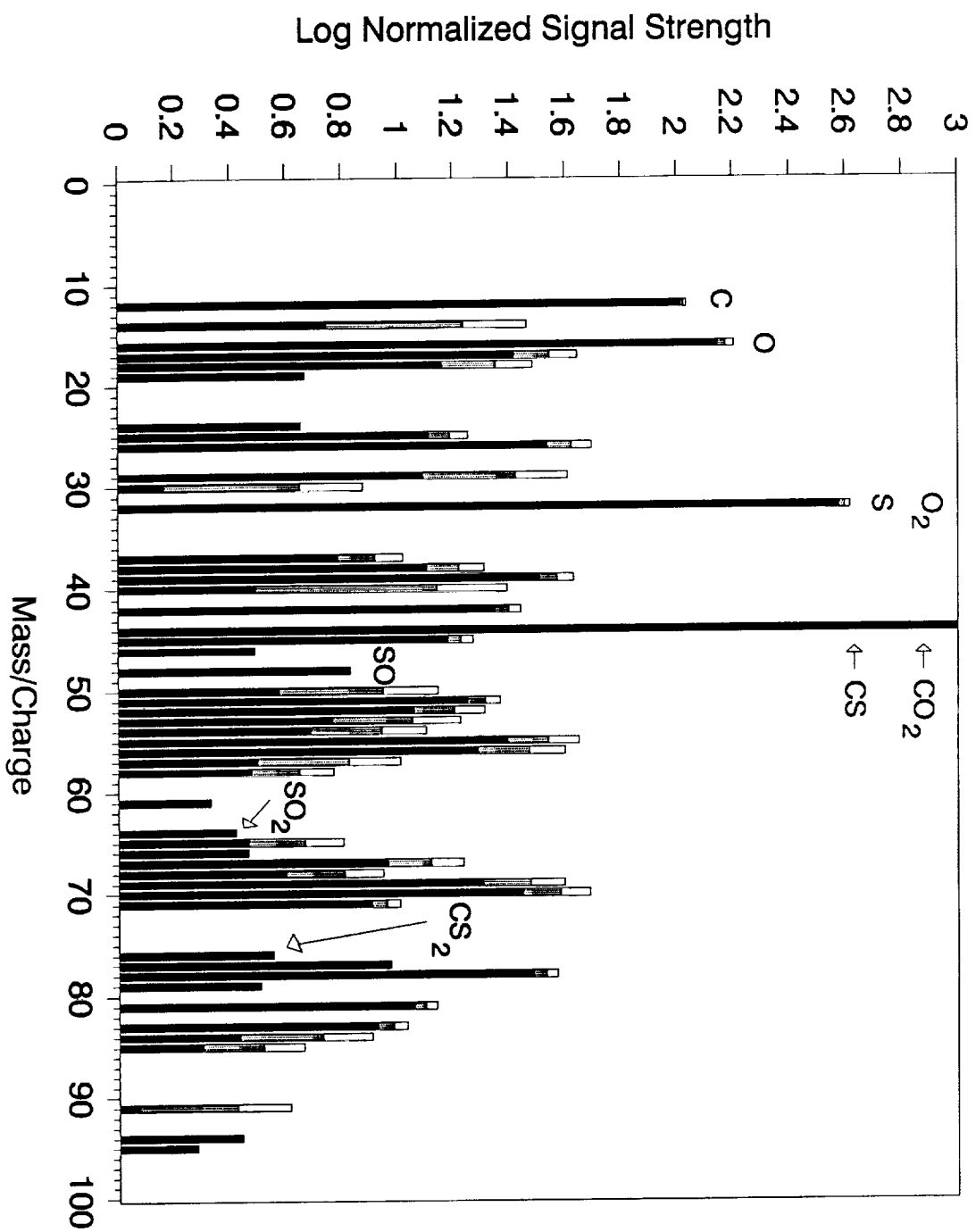
TROILITE

On Gold Coated with Silicone Oil

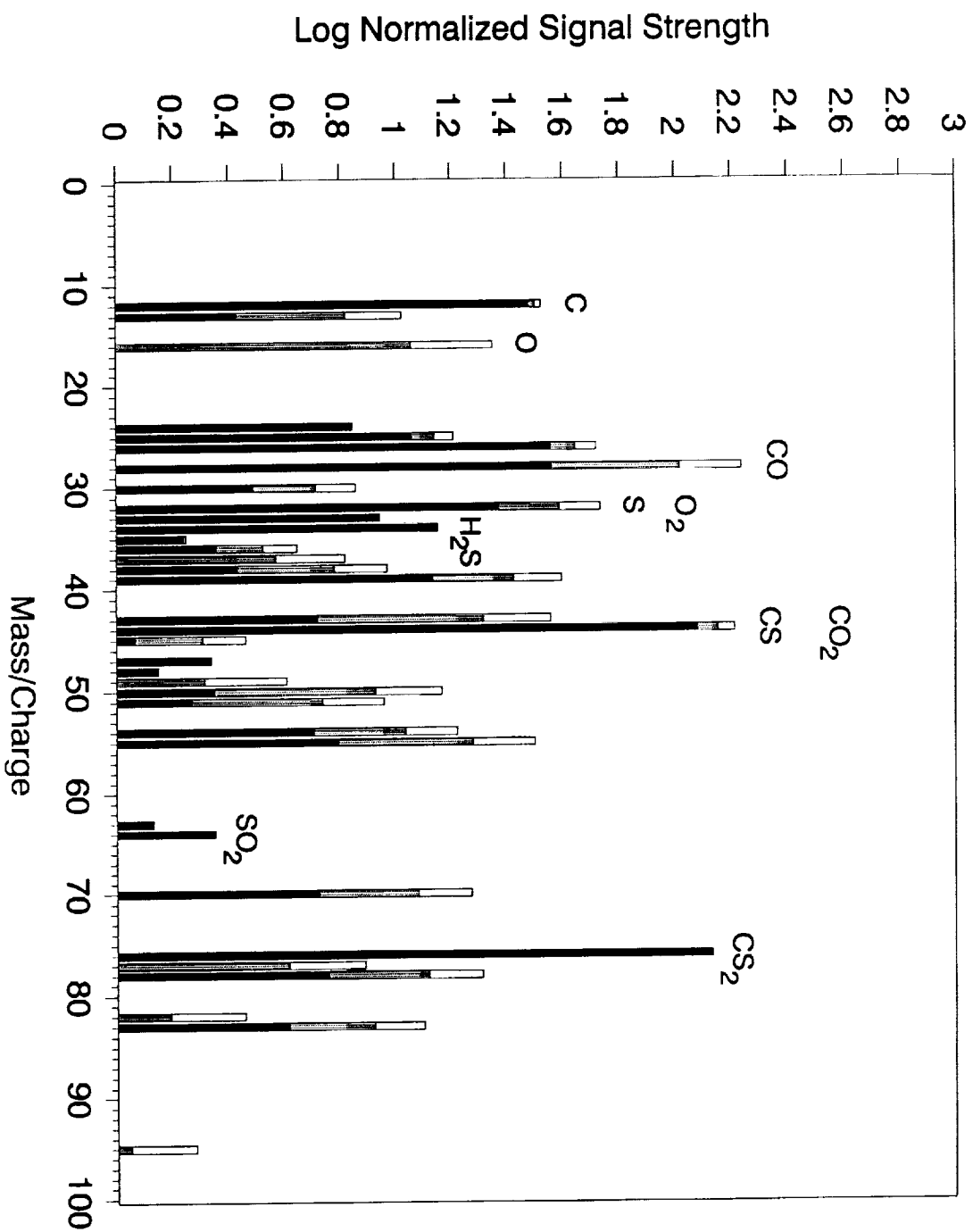


TROILITE

On Gold Rinsed with Hexane

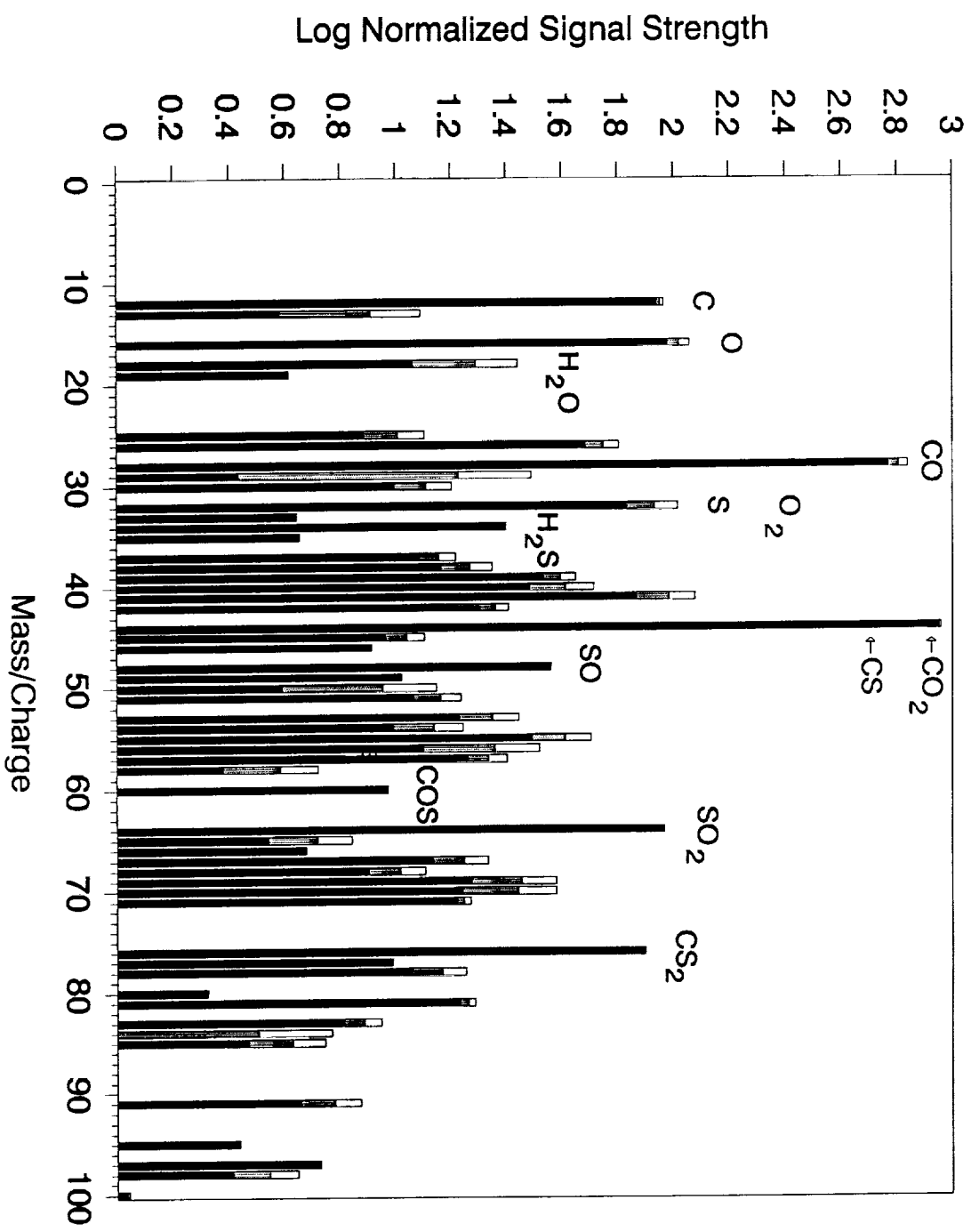


AZURITE, CALCITE, AND TROILITE MIXTURE On Gold Coated with Silicone Oil



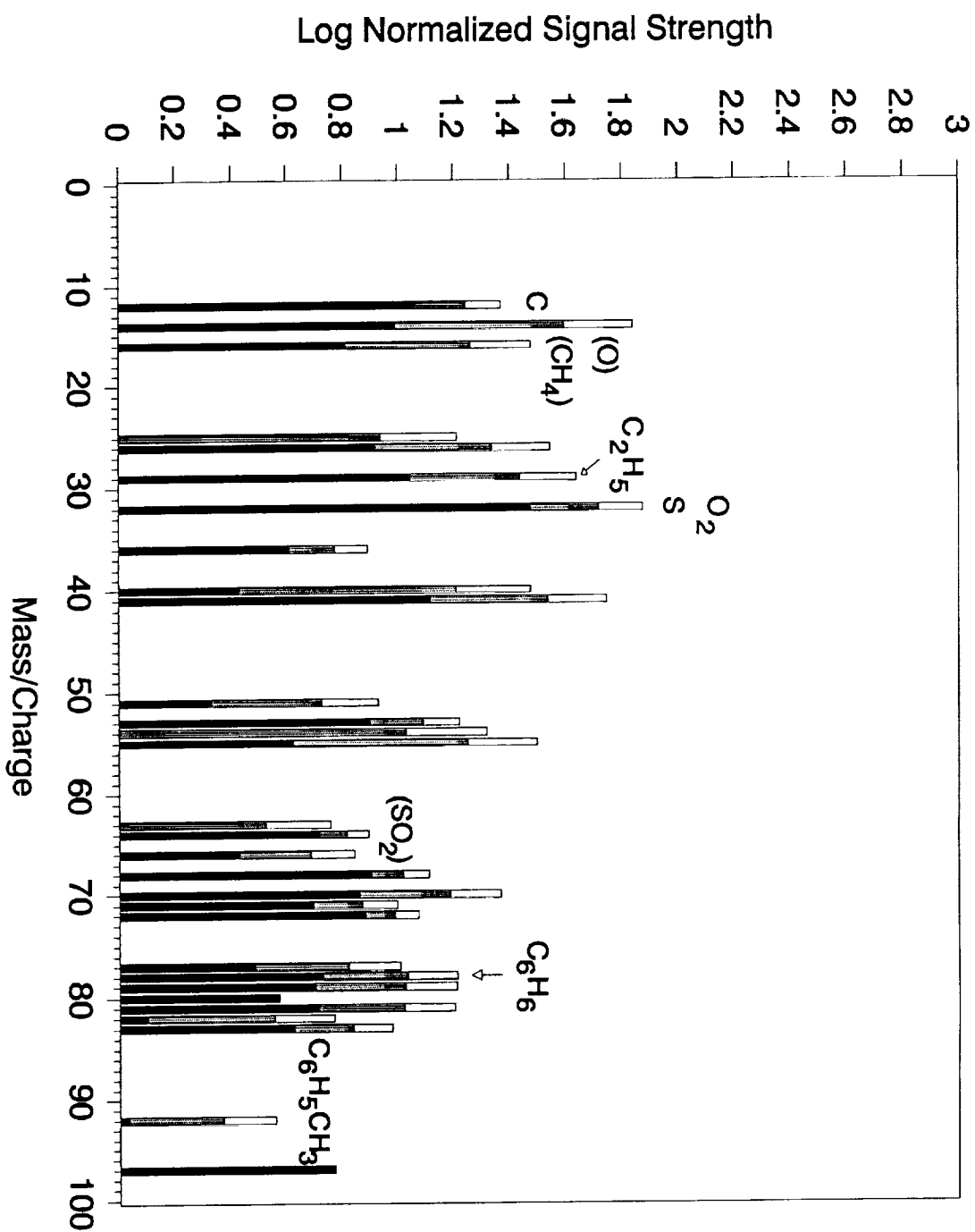
AZURITE, CALCITE, AND TROILITE MIXTURE

On Gold Rinsed with Hexane



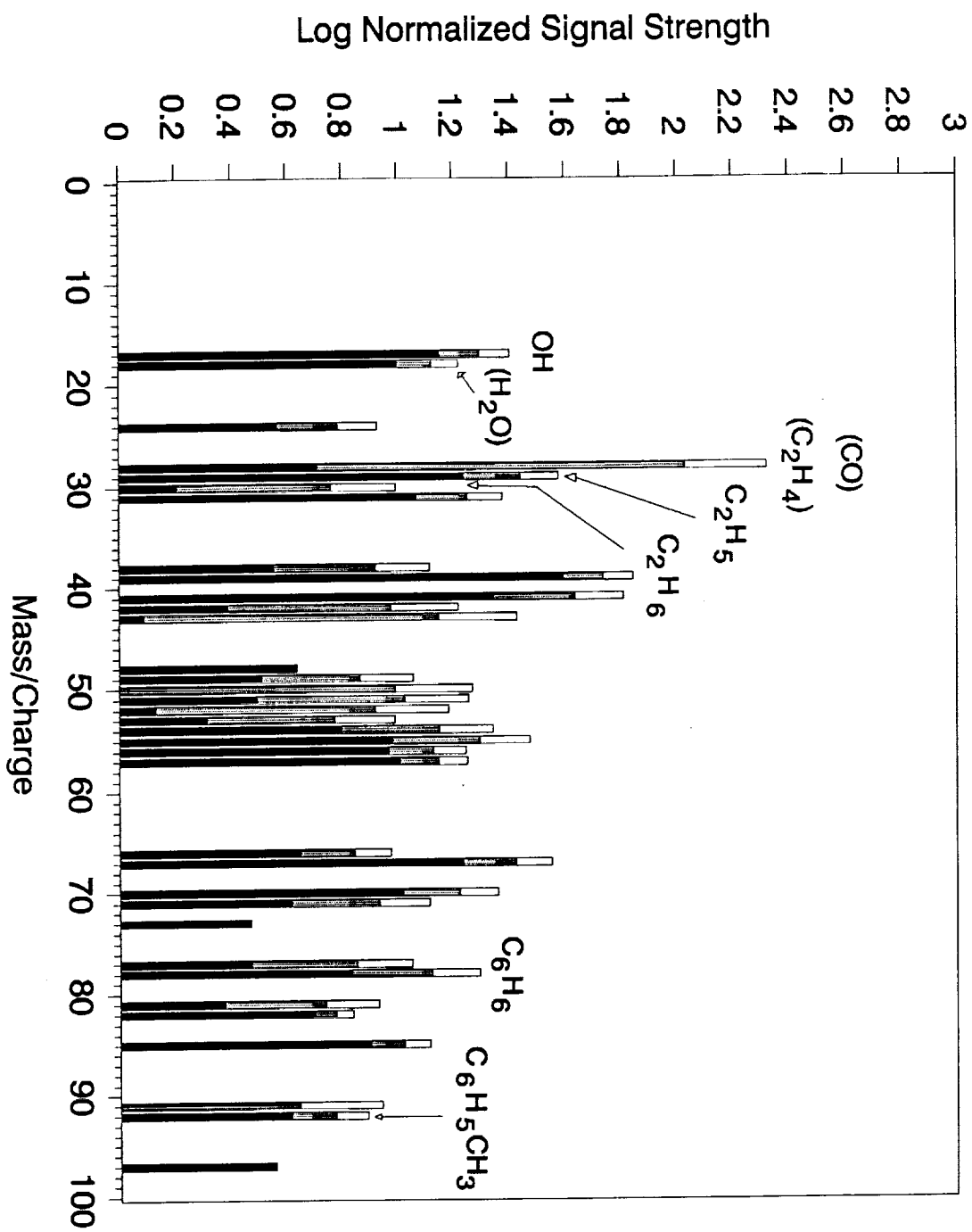
PARTICLE L2005C21

On Gold



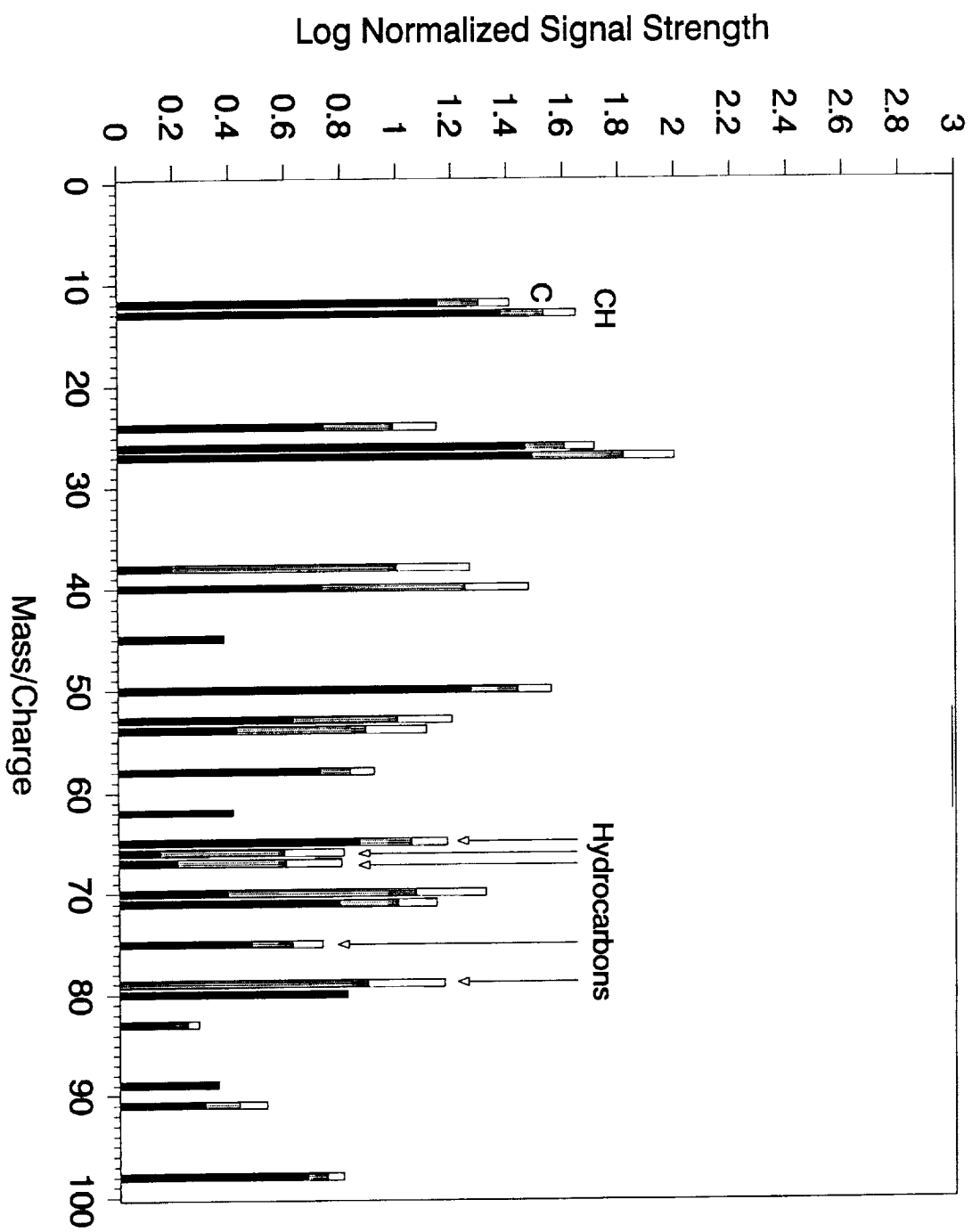
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On Gold



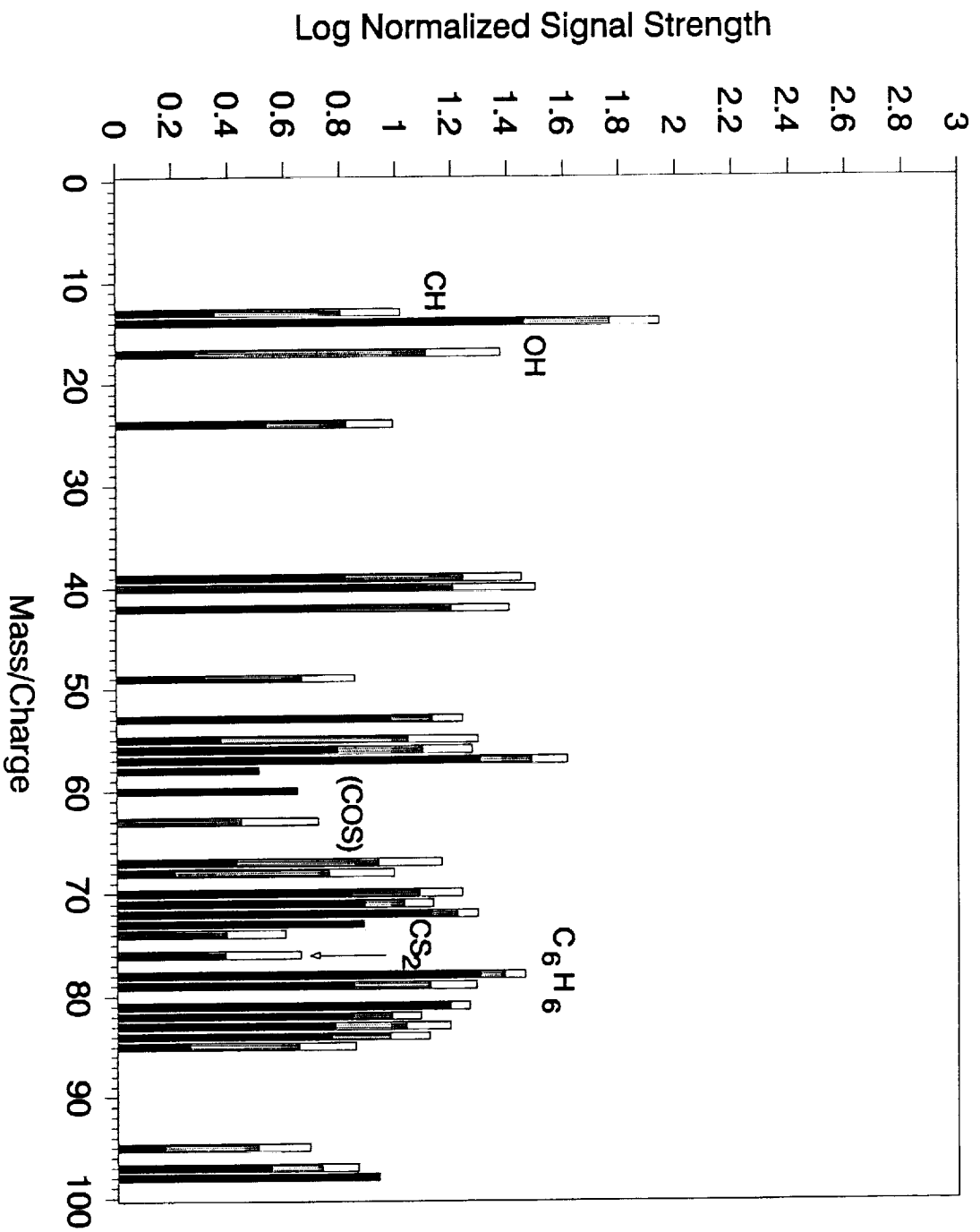
PARTICLE L2005C26

On Gold



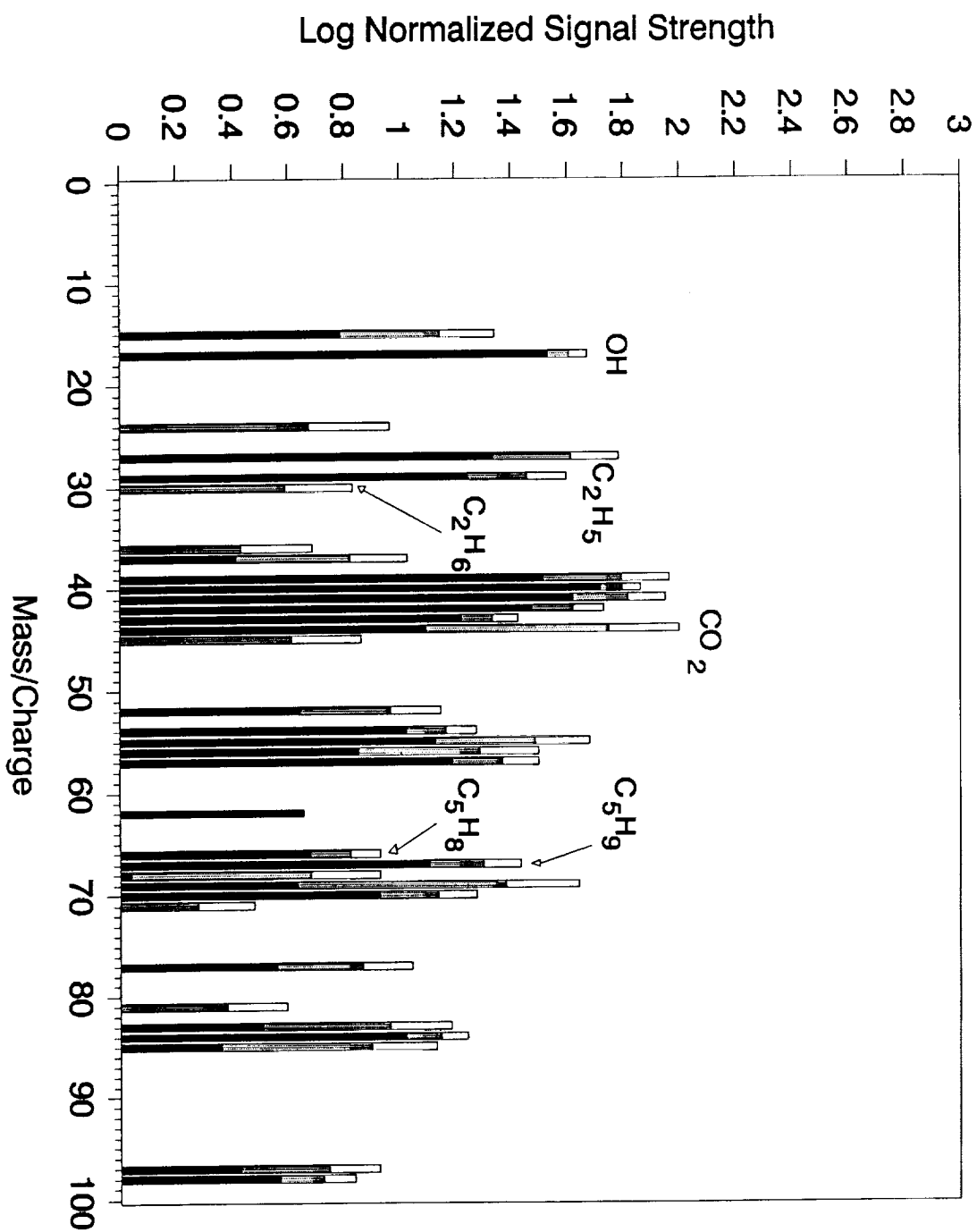
PARTICLE L2005C28

On Gold



PARTICLE L2005C30

On Gold



PARTICLE L2005D27

On Gold

